MODELING CHEMICALLY REACTIVE AIR TOXICS IN THE SAN FRANCISCO BAY AREA USING CAMx

Chris Emery, Greg Yarwood, Ed Tai, Ralph Morris
ENVIRON International Corporation
Novato, CA

Phil Martien and Saffet Tanrikulu
Bay Area Air Quality Management District
San Francisco, CA

October 6, 2008

Introduction

- Under its Community Air Risk Evaluation (CARE) Program, BAAQMD is developing:
  - Annual/gridded toxics emissions inventory
    - 9-county area on 2-km grid
    - Diesel PM and reactive gasses (benzene, butadiene, acrolein, etc.)
  - Multi-scale toxics modeling system
- Purpose of this initial modeling application
  - Develop a CAMx modeling capability
  - QA preliminary toxics emissions inventory
  - Refine method for seasonal/annual modeling in the future

Introduction

- Initial application approach:
  - Episode of opportunity:
    - July 29-Aug 1 2000 CCOS episode
    - Existing CARB 4-km Central California modeling grid
    - Existing CARB MM5 meteorology
    - Existing CARB SAPRC99 photochemical inventory
  - Run CAMx with the Reactive Tracer (RTRAC) tool
    - Use preliminary Bay Area (9-county) toxics inventory
    - Compare basic vs. detailed toxics chemistry mechanisms

CAMx Reactive Tracer Tool

- CAMx core model addresses:
  - Emissions, dispersion, deposition, photochemistry (ozone and PM)
  - Gas-phase chemistry is CB4, CB05, or SAPRC99
- RTRAC treats:
  - Reactive tracers (e.g., toxics) with user-defined chemistry
  - Oxidants are extracted from the standard CAMx photochemical mechanisms

CAMx Reactive Tracer Tool

- Reactive Tracer Chemical Mechanism Compiler (RTCMC)
  - An extension of RTRAC that allows much more chemistry detail
  - Reads and solves a user-defined chemistry mechanism among tracers and core model species
    - Current implementation is for gas-phase reactions only
    - Assumes tracers have no feedback on core species
  - RTCMC automation allows for significant detail quickly, easily, and accurately

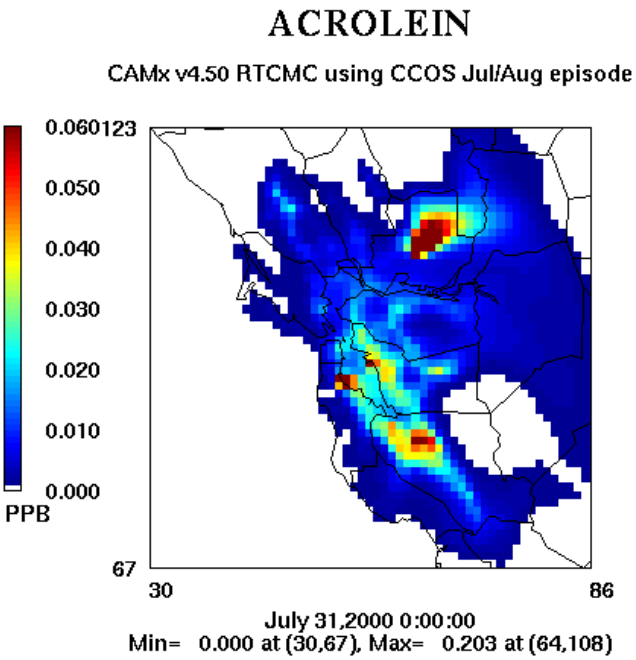
Bay Area Toxics Modeling

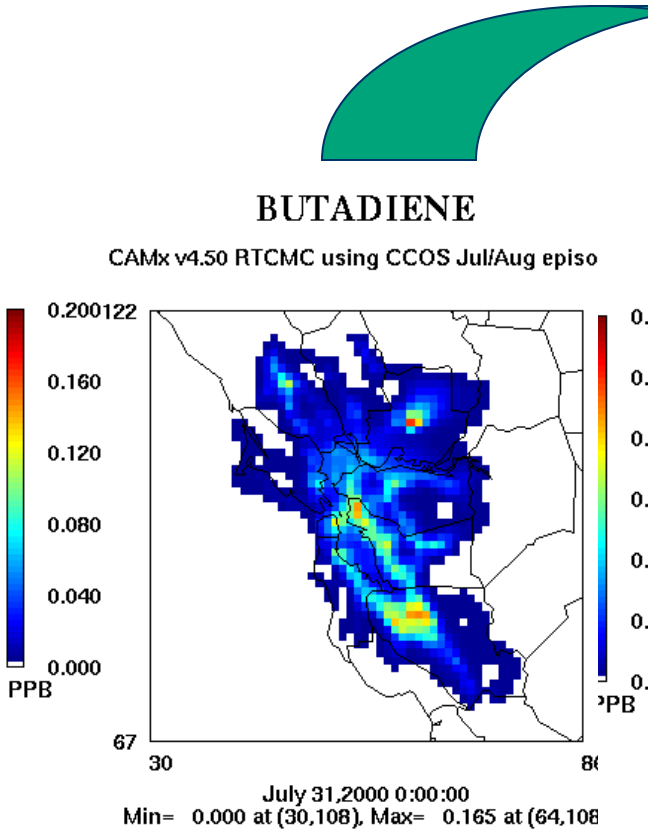
- Two levels of chemistry were investigated using RTCMC:
  - Basic: 3 reactive tracers, 12 reactions
  - Detailed: 27 reactive tracers, 59 reactions
- Basic butadiene/acrolein mechanism
  - Comparable to CMAQ's CB05+toxics chemistry
  - Primary butadiene
    - Decays by O3, NO3, OH, O (from SAPRC99)
  - Primary acrolein
    - Decays by photolysis, O3, NO3, OH (from SAPRC99)
  - Secondary acrolein from butadiene
    - Decays by photolysis, O3, NO3, OH (from SAPRC99)

RTCMC Input File for Basic Mechanism

```
#Control
    rate_species_units = 'molecules/cm3'
    rate_time_units = 'sec'
    solver = 'dlsode'
    Jacobian = 'numeric'
#Species,Type,Ambient,Tolerance,deposition vel,wet scav,mw,ldos,ldep
O3         A           1.0               1.0E-12      0.0      0.0  1.0
OH         A           1.0               1.0E-12      0.0      0.0  1.0
NO3        A           1.0               1.0E-12      0.0      0.0  1.0
O          A           1.0               1.0E-12      0.0      0.0  1.0
BUTADIENE  F           1.0               1.0E-12      0.0      0.0 54.09
ACROLEINE  F           1.0               1.0E-12      0.0      0.0 56.06
SEC_ACRO   F           1.0               1.0E-12      0.0      0.0 56.06
#Table
  0         0.        10.        20.        30.        40.        50.        60.        70.        78.        86.
  8  5.158E-04  5.105E-04  4.937E-04  4.648E-04  4.223E-04  3.633E-04  2.843E-04  1.830E-04  9.297E-05  2.472E-05
 12  5.158E-04  5.105E-04  4.937E-04  4.648E-04  4.223E-04  3.633E-04  2.843E-04  1.830E-04  9.297E-05  2.472E-05
#Equations
  1 [BUTADIENE] + [OH]    -> [SEC_ACRO] ;  2  1.400E-11   424.  0.
  2 [BUTADIENE] + [O3]    -> [SEC_ACRO] ;  2  8.200E-15 -2070.  0.
  3 [BUTADIENE] + [NO3]   -> [SEC_ACRO] ;  1  1.790E-13
  4 [BUTADIENE] + [O]     -> [SEC_ACRO] ;  2  1.030E-15     0. -1.45
  5 [ACROLEIN]  + [OH]    ->            ;  1  2.000E-11
  6 [ACROLEIN]  + [O3]    ->            ;  1  2.610E-19
  7 [ACROLEIN]  + [NO3]   ->            ;  2  1.700E-11 -3131.  0.
  8 [ACROLEIN]            ->            ;  0
  9 [SEC_ACRO]  + [OH]    ->            ;  1  2.000E-11
 10 [SEC_ACRO]  + [O3]    ->            ;  1  2.610E-19
 11 [SEC_ACRO]  + [NO3]   ->            ;  2  1.700E-11 -3131.  0.
 12 [SEC_ACRO]            ->            ;  0
```

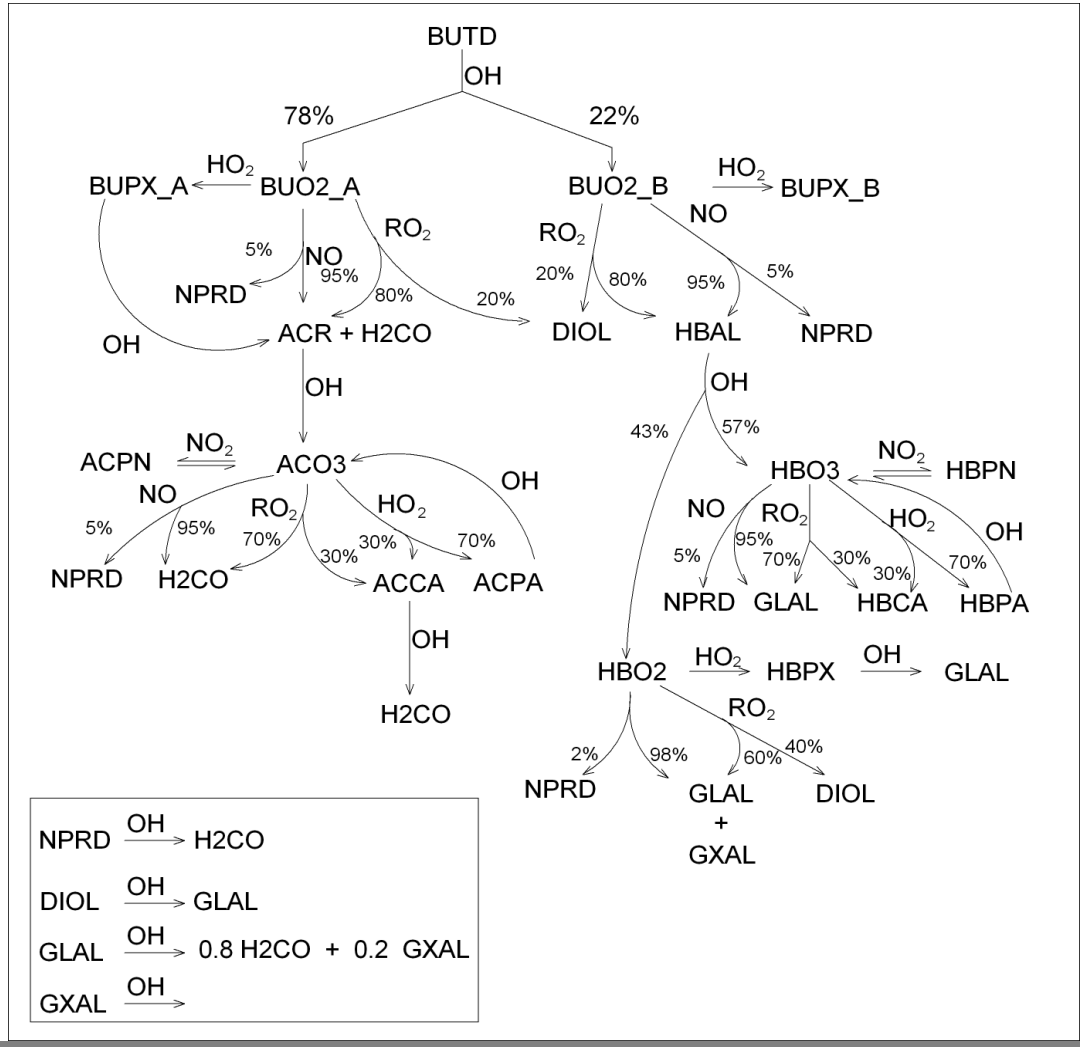
Results from Basic Mechanism





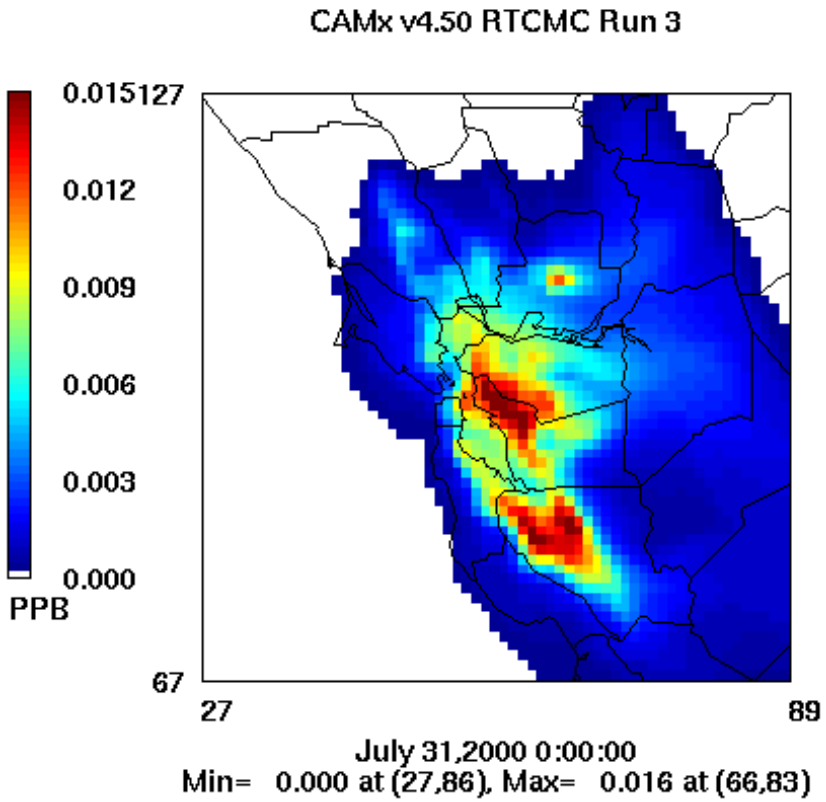
Detailed Butadiene/Acrolein Mechanism

- 27 species, 59 reactions
  - Condensed from MCM version 3.1
- Acrolein and formaldehyde are chemically formed (no emissions)
- Adds benzene and its decay

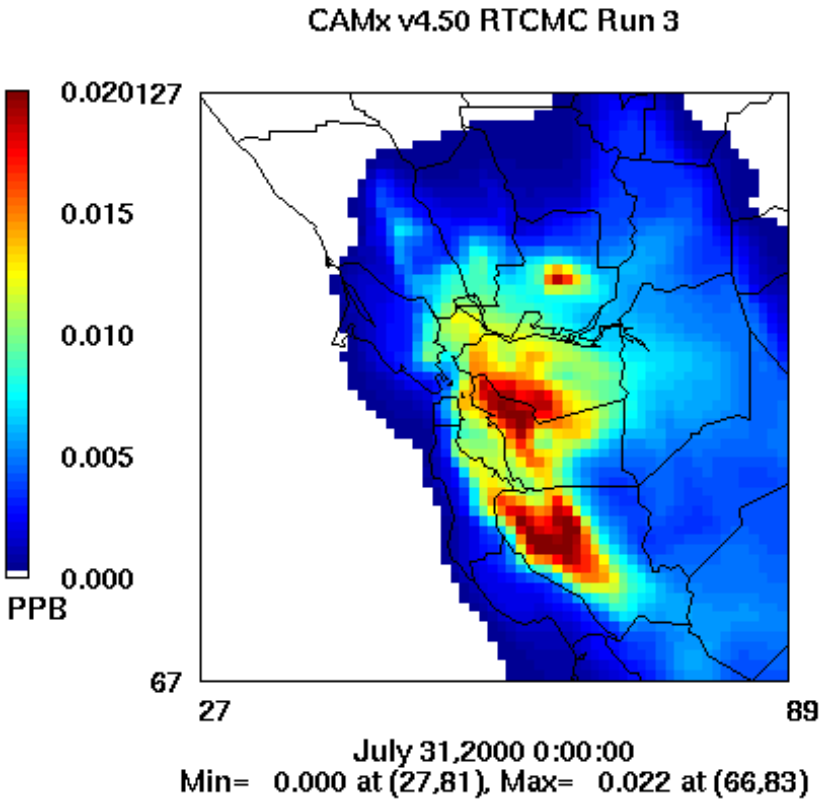


Results from Detailed Mechanism

Secondary Acrolein from Butadiene

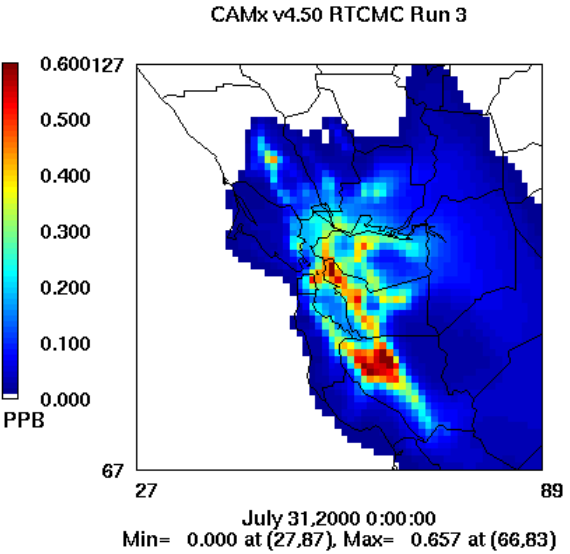


Secondary Formaldehyde from Butadiene

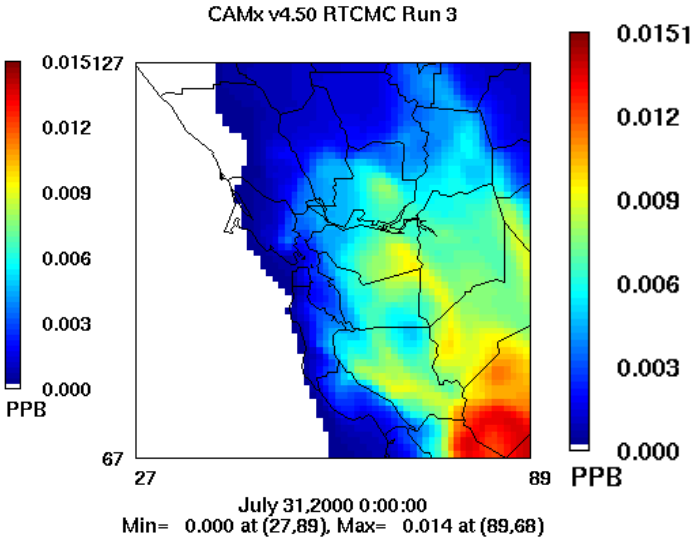


Results from Detailed Mechanism

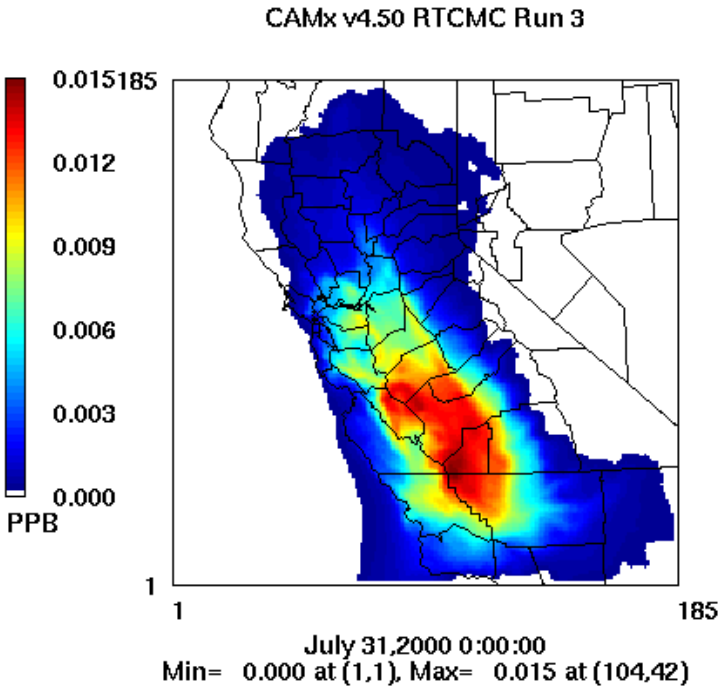
Primary Benzene



Reacted Benzene



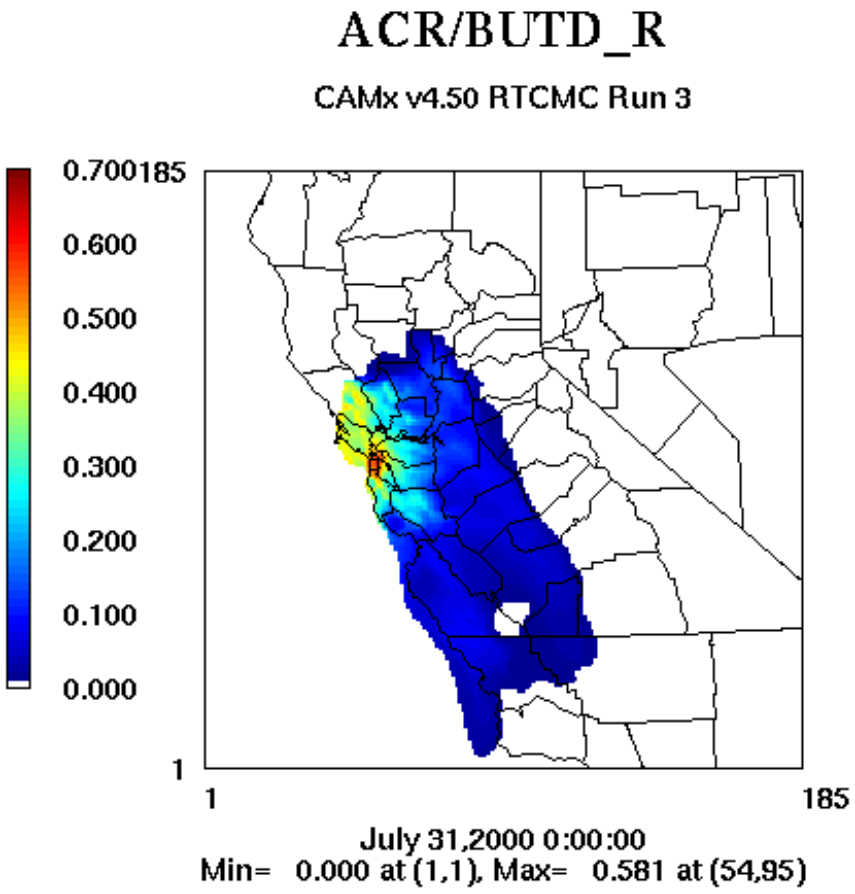
Reacted Benzene

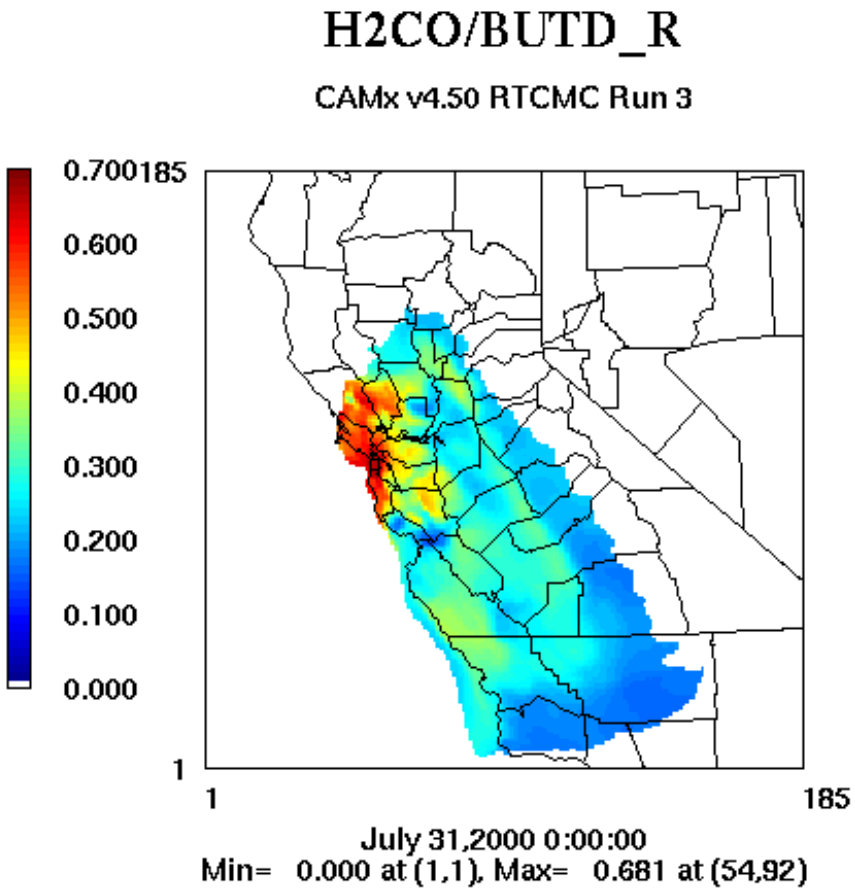


Results from Detailed Mechanism

- Analysis of fractional yields:
  - [ACR] / [BUTD_R] is the net yield of acrolein from butadiene
    - Accounts for only the acrolein that is present
    - BUTD_R is the total butadiene reacted
  - [H2CO] / [BUTD_R] is the net yield of formaldehyde from butadiene
    - Accounts for only the formaldehyde that is present

Results from Detailed Mechanism

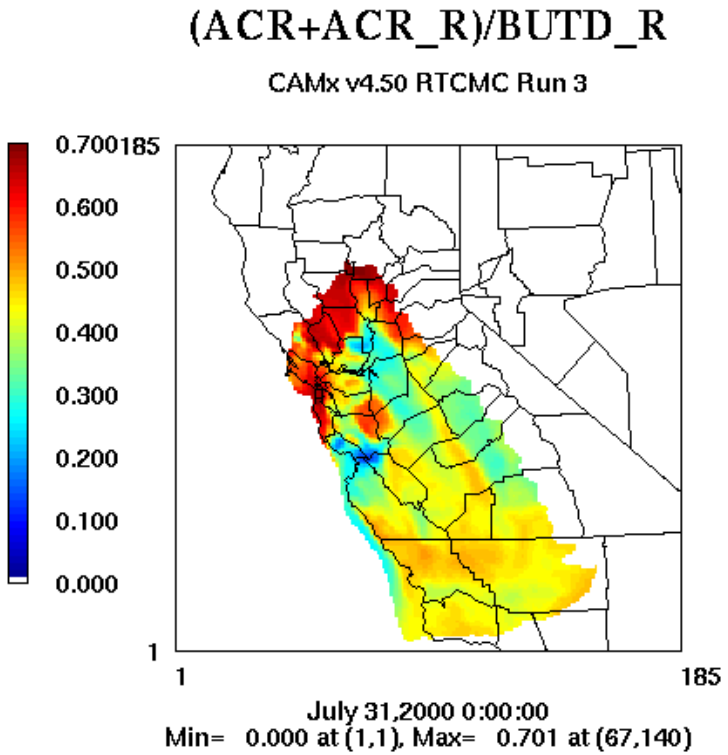




Results from Detailed Mechanism

- Analysis of fractional yields:
  - [ACR + ACR_R] / [BUTD_R] is the total yield of acrolein formed from butadiene
    - Accounting for the fact that acrolein also decays once it is formed

Results from Detailed Mechanism



- Yield in the basic mechanism is 1 (BUTD $\rightarrow$ 1 ACR)
- Yield in the detailed mechanism is 0.4-0.7, and is VOC:NOx dependent

Conclusion

- Results are preliminary, but provide useful information
  - Efforts to add toxics into SAPRC99 or CB05 tend toward basic mechanisms with limited interactions
  - But differences in the chemical detail can have important ramifications
    - E.g., the basic butadiene/acrolein simulation over estimates secondary acrolein yield
  - RTCMC allows significant detail quickly and easily with commensurate improvements in mechanism accuracy